



The electronic structure of zirconium in hydrided and oxidized states



Hamed Akhiani^{a,*}, Adrian Hunt^b, Xiaoyu Cui^c, Alexander Moewes^b, Jerzy Szpunar^a

^a Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Canada

^b Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada

^c Canadian Light Source, Saskatoon, Canada

ARTICLE INFO

Article history:

Received 21 February 2014

Received in revised form 19 August 2014

Accepted 9 October 2014

Available online 19 October 2014

Keywords:

Zirconium

Zirconium oxide

Zirconium hydride

XPS

XANES

ABSTRACT

Valence band energy shifts for pure zirconium and a model zirconium alloy (Zircaloy-4) in oxidized and hydrided states have been investigated with X-ray photoelectron spectroscopy (XPS) and X-ray Absorption Near-Edge Structure (XANES) technique. With XANES, we show that O/H interactions in oxidized Zr can be detected in the near-edge region of O K. Using density functional theory (DFT) simulations, we have determined where H atoms bond in the monoclinic ZrO₂ lattice. The preferred stoichiometry is ZrO₂:H, but the O–H bond is weak; increasing H causes the H atoms to form H₂ molecules rather than O–H bonds. These interactions cause energy shifts in the Zr 3d XPS spectra. The results illustrate the complex processes of hydrogen and oxygen interactions at the Zr surface.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Zirconium and its alloys are among the materials that are widely used in nuclear reactors as structural materials. The main advantage of these alloys is their exceptional combination of neutron transparency, oxidation behavior and mechanical properties at the service temperatures. Pure Zr and Zr alloys can form a spontaneous oxide layer on their surface. This layer protects against further oxidation and is similar to that formed on the surface of aluminum and titanium based alloys [1]. Inhibiting further oxidation and hydriding of Zr-alloys used in nuclear reactors is a crucial design consideration, because these chemical reactions cause the brittleness and the interior mechanical stresses within the fuel rods to increase, which may lead to premature failure and rupture of the fuel cladding. Understanding the structural changes that Zr alloys undergo is therefore critical from the standpoint of nuclear reactor safety.

The protectiveness of this oxide layer depends on its morphology and crystal structure [2,3]. Zirconium oxide, known as zirconia, has three common allotropes; monoclinic, cubic and tetragonal. Monoclinic and tetragonal allotropes are stable below and above 1000 °C, respectively. After lengthy oxidation at temperatures above 1900 °C, cubic, trigonal and pseudo-hexagonal structural modifications have been reported [4]. Therefore, monoclinic and tetragonal oxides are the phases of zirconia that will most likely form within in a nuclear reactor during service.

Zirconia is used for many applications besides nuclear fuel claddings, such as thermal barrier coatings, refractory materials, biomaterials manufacturing, and jewelry. Due to the wide application range of zirconia and its allotropes, characterizing the various types of zirconia is of a great importance and interest to these other industries, as well as the nuclear power industry.

There are many literatures on ZrO₂ formation, micro structure, texture, and allotropes. Most of these studies are based on X-ray diffraction and Raman spectroscopy. In this study, synchrotron radiation at the Canadian Light Source (CLS) has been used to study the Zr oxide and hydride structure. X-ray photoemission spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) techniques are used to follow the changes in electronic structure of Zr before and after oxidation and hydriding of pure Zr and a model Zr alloy (Zircaloy-4).

2. Materials and methods

To study the effects of oxidation and hydriding on pure Zr and Zircaloy-4, commercially pure Zr 702 (99.8%, All-chemie LTD) and Zircaloy-4, with the composition of 1.45 wt% Sn, 0.24 wt% Fe, 0.13 wt% Cr, 0.1 wt% O, and balanced Zr, were used in this study. Four samples of pure Zr, not including the control, are listed in Table 1. Pre-oxidizing of the samples was performed in a tube furnace at 400 °C for 24 h. In addition, one Zircaloy-4 sample has been oxidized for one hour to illustrate the effect of a thin oxide layer in the XPS spectra (Fig. 3). Similarly, hydriding was done in the same furnace at 400 °C under Ar-2.5% H₂ atmosphere for 3 h. The samples were then furnace cooled, cut into approximately 5 mm × 5 mm pieces and ultrasonically cleaned with methanol for 5 min prior to the experiments. In order to reveal the hydrides on the surface and characterize them by Electron Backscattered Diffraction (EBSD), one of the hydrided samples was etched by an acidic solution consisting of HF:HNO₃:H₂O = 1:10:10.

* Corresponding author.

Table 1
Pure zirconium samples preparation condition.

Sample name	Description	Treatment procedure
Zr	Pure Zr	
Zr. hyd	Pure Zr + Hydrided	Hydriding at 400 °C in Ar-2.5% H ₂ for 3 h
Zr. hyd. e	Pure Zr + Hydrided + etched	Hydriding at 400 °C in Ar-2.5% H ₂ for 3 h + surface etching by an acidic solution
Zr. ox	Pure Zr + Preoxidized	Pre-oxidizing at 400 °C in air for 24 h
Zr. hyd. ox	Pure Zr + Preoxidized + Hydrided	Pre-oxidizing at 400 °C in air for 24 h + Hydriding at 400 °C in Ar-2.5% H ₂ for 3 h

Four samples of Zircaloy-4, not including the controls, were also prepared. Table 2 shows the Zircaloy-4 sample conditions. For Zircaloy-4 samples, two different surface roughness as well as pre-oxidized and hydrided states were studied. The two surface roughness were 1) as received sample (P) with $R_a = 0.2 \mu\text{m}$ and 2) G sample with $R_a = 2.79 \mu\text{m}$ which was ground in our laboratory using 60 grit SiC abrasive paper. Our previous work [5,6] showed that increasing the surface roughness will increase the weight gain of Zircaloy-4 samples, however the oxidation rate is almost the same. Thus we seek to understand if the surface roughness can induce any changes to Zr electronic states on the surface that experienced both oxidizing and hydriding regimes.

To characterize the electronic structure of all of the samples, X-ray photoemission spectra (XPS) were measured at the PGM beamline at the Canadian Light Source (CLS). The PGM beamline utilizes a Variable Line Spacing Plane Grating Monochromator (VLS PGM). This beamline is optimized for flux in the energy range between 5 and 250 eV. All spectra were performed with the Scienta SES100 analyzer with a total energy resolution of 40 meV under 10^{-10} Torr vacuum.

In addition to the XPS measurements, Zr $M_{4,5}$ XANES spectra were also measured at the PGM beamline; with a resolving power $E/\Delta E$ greater than 10,000, the energy resolution of the spectrometer on the PGM beamline at the Zr $M_{4,5}$ edge is 20 meV. Oxygen K spectra were recorded at the RIXS end station of the REIXS beamline [7]. The resolution on the O K edge is 50 meV. Spectra were collected using the total fluorescence yield (TFY) and total electron yield (TEY) detection schemes.

Simulations of the XANES spectra were accomplished using WIEN2k, which is a DFT-based code that utilizes a full-potential muffin-tin approach when it calculates the electronic structure. The 'muffin tins' are spherical regions of space that surround each atom, and contain the core electrons as well as some of the valence states. The state of the core electrons is explicitly solved using an atomic Hamiltonian, which gives WIEN2k its status as a full-potential code. However, the Kohn-Sham equations are solved to find valence and conduction band states using a linearized augmented plane wave (LAPW) basis set. The Kohn-Sham equations are solved in reciprocal space on a grid within the irreducible part of the Brillouin zone. Higher symmetry cells thus require few k -points.

The final state of an atom after an X-ray absorption event has a hole in the core level. This core hole perturbs the local states sufficiently that the system can no longer be considered in the ground state, and the excited state must be explicitly modeled for accuracy. To model the core hole effect, we constructed a $2 \times 2 \times 2$ super cell, then placed a core hole at one of the non-equivalent sites in that cell. We also added a background charge to conserve the charge within the super cell. This typically reduced the symmetry dramatically. A calculation was then allowed to proceed as normal, albeit with a core hole and background charge. This process was repeated for all non-equivalent sites, and the results of each simulation were added together with appropriate weighting to account for multiplicity of each site.

In order to validate the presence of hydride phase, some XRD measurements along with EBSD imaging of structure were performed. Monoclinic ZrO_2 , tetragonal ZrO_2 , ZrH_x (where $1 < x < 2$) and zirconium were identified, respectively using JCPD 037-1484, 01-080-0784, 034-0649 and 005-0665. XRD studies were done with a Bruker D8 X-ray diffractometer using $\text{Cu K}\alpha$ with 0.5 mm collimator and 3 mm oscillation on the plane of sample. EBSD imaging was done with Oxford hardware and HKL software installed on Hitachi SU-6600 FE-SEM.

3. Results and discussion

3.1. XPS analysis

Zr 3d photoemission spectra were obtained for all pure Zr and Zircaloy-4 samples. Fig. 1 shows the Zr 3d XPS spectra of pure Zr

Table 2
Zircaloy-4 samples preparation condition.

Sample code	Surface roughness $R_a \pm 0.02$ (μm)	Treatment procedure
Zrly	0.20	
G	G2	Pre-oxidized (400 °C/24 h/air) + Hydrided (400 °C/3 h/Ar-2.5% H ₂)
	G4	Hydrided (400 °C/3 h/Ar-2.5% H ₂)
P	P2	Pre-oxidized (400 °C/air/24 h) + Hydrided (400 °C/3 h/Ar-2.5% H ₂)
	P4	Hydrided (400 °C/3 h/Ar-2.5% H ₂)

samples with different conditions that were stated in Table 1. The control sample (pure Zr: black curve in Fig. 1) shows a doublet at 182.5 and 184.9 eV. These energies coincide well with the Refs. [8–10]. Pure Zr which has been pre-oxidized (green curve in Fig. 1) shows a 1 eV shift toward higher binding energy, which is corresponding to the formation of Zr bonds with oxygen. Pure Zr sample with hydrides (blue curve in Fig. 1), shows almost no shift compared to pure Zr. The penetration depth of electrons in this kinetic energy range is around few Å. It could be that most of the ZrH_x does not exist near the surface. After etching the surface of the hydrided sample (yellow curve in Fig. 1), a slight shift toward higher binding energy can be observed in this sample. Interestingly, the sample which has been pre-oxidized and then hydrided shows a significant shift (~ 4 eV). The detailed discussion will be shown later in Sections 3.3 and 4.

We also acquired the Zr 3d spectra for the treated Zircaloy-4 samples as noted in Table 2. Fig. 2 illustrates the Zr 3d XPS for the treated (G2, G4, P2, P4) Zircaloy-4 samples. The Zr 3d states of the pre-oxidized samples, namely P2 (blue curve) and G2 (black curve), have an energy shift relative to the non-oxidized samples P4 (green curve) and G4 (red curve).

To compare the Zr 3d doublet in pure Zr and Zr model alloy (Zircaloy-4), we measure the Zr 3d spectra for Zircaloy-4. Moreover, to illustrate the role of thin oxide layer in Zircaloy-4, we acquired XPS spectra of pre-oxidized Zircaloy-4. Fig. 3 illustrates the Zr 3d states of as-received and pre-oxidized (400 °C/1 h) Zircaloy-4 samples. In Fig. 3a, the spectra of the as-received sample are analysed by three sets of doublets. The former set was positioned at 179.6 and 181.0 eV, which is the characteristic Zr 3d doublet [10]. The latter set was shifted by about 3 eV (183 and 185.1 eV) and this shift is characteristic for ZrO_2 . This is very close to the position that we measured for the pure Zr sample (Fig. 1). The middle doublet could be related to the formation of non-stoichiometric zirconium oxides. In contrast to these doublet sets, only one doublet presents in the pre-oxidized Zircaloy-4 sample (Fig. 3b). Perhaps this can be related to the oxidation state of Zr^{4+} which will be discussed later in Section 4.

As mentioned before, due to the surface sensitivity of the photoemission technique, even a very thin oxide layer of native ZrO_2 can be detected. This fact along with low oxidation resistance of pure Zr leads to shifted positions of Zr 3d in the pure Zr samples.

3.2. XANES analysis

X-ray absorption near-edge spectroscopy (XANES) is a technique that one may use to obtain detailed information about the chemical environment of a certain element within a material.

Download English Version:

<https://daneshyari.com/en/article/1609919>

Download Persian Version:

<https://daneshyari.com/article/1609919>

[Daneshyari.com](https://daneshyari.com)